CLAIMS

1. Semi-permeable multi-hollow fibre, characterised in that the hollow fibre (1, 3) has several separated hollow sections (2) which extend along the overall length of the hollow fibre (1, 3) and each have a full-length through hole.

2. Semi-permeable hollow fibre according to claim 1 characterised in that the numerous hollow sections (2) are provided in one hollow fibre (1).

3. Semi-permeable hollow fibre according to claim 1 characterised in that several hollow fibre units (1) which each have a circular cross-section are connected to one another along the fibre axes by way of a connecting section (1a) to form one piece.

4. Semi-permeable hollow fibre according to claim 3 characterised in that the numerous hollow fibres (1) which each have a circular cross-section are stuck or joined with direct action with one another along the fibre axes.

5. Method for manufacturing a semi-permeable hollow fibre characterised in that a solution (21) of a composition of high molecular weight which is dissolved in a solvent is extruded through several ring slits (7), and that the threads (3) thus extruded are gathered in a state in which the hollow fibres (1) can be actively connected.

6. Method according to claim 5 characterised in that the extruded threads (3) are gathered in a coagulating bath.

7. Method according to claim 5 characterised in that the extruded threads (3) are gathered in a hydrolyzing bath (23).

8. Method according to claim 5 characterised in that the extruded threads (3) are gathered in a plasticizing bath.

9. Method according to one of claims 5 to 8 characterised in that several hollow fibres (1) are brought during and/or after their assembly into contact with a solvent or

an expanding agent for the composition of high molecular weight which is used during the fibre formation.

10. Spinning nozzle for manufacturing the semi-permeable hollow fibre characterised in that the spinning nozzle has several openings (5) independent of one another for injection of a first fluid (20) and a corresponding number of ring slits (7) which surround the individual openings (5) wherein the ring slits (7) are connected to one another to form one continuous slit (9) for extruding a fibre-forming material (21).

11. Spinning nozzle according to claim 10 characterised in that the openings (5) for injection of the first fluid (20) are arranged symmetrically or in a row, and that at least one slit-like passage (9) is provided in the one or several spaces between the openings (5) to connect the ring slits (7) for extrusion of the second fluid or fibre-forming material (21).

12. Spinning nozzle according to claim 11 characterised in that the at least one slit-like passage (9) is enlarged in the centre ( Figures 10, 11).

<u>Semi-permeable multi-hollow fibre, method for its manufacture and spinning nozzle usable therefor</u>

The invention relates to a semi-permeable hollow fibre, and more particularly a multi-hollow fibre with selective permeability, a method for its manufacture and to a spinning nozzle which can be used for such a method.

A hollow fibre blood dialyser (dialysis machine) has already been developed as an artificial kidney and is used increasingly in the therapy treatment of kidney patients. However as the therapy treatment advances so a higher degree of efficiency in the hollow fibres is sought by the relevant parties in the field of medicine. Even if an effective artificial kidney with hollow fibres is used it is necessary for the patients to undertake haemodialysis (blood dialysis) several times a week, namely seven to eight hours on average at the present time. To reduce the burden for the patient a short-term haemodialysis is therefore urgently required. Furthermore it should not be overlooked that haemodialysis patients have a higher mortality risk than a generally healthy person. The urgency mentioned above is therefore even more pressing. The build-up of so-called mean molecules whose molecular weight is assumed in a range between 1.000 and 5.000, is regarded at the present time as most suspect. It is thus important to improve the degree of efficiency of hollow fibres as regards removing these mean molecules. Taking into consideration that the blood volume outside of the body during therapy represents a significant physical strain for the patient it is necessary to reduce both the side volume of the artificial kidney and also the blood volume outside of the body. To meet these demands it has to be seen as very desirable if a hollow fibre membrane is improved both with regard to its effectiveness and its degree of efficiency.

The hollow fibre membrane which is used for haemodialysis is generally only 8 – 30 μm thick and has an external diameter of 100 – 300 μm. Therefore mechanical damage can easily occur. This means that the handling of hollow fibres during the assembly of the haemodialyser has to be carried out with great care and attention. Even a slight mechanical contact can damage the hollow fibre which can be the cause of blood leaks when the haemodialyser is in use. The handling of the hollow fibre

therefore requires extraordinary work and nervous effort. On the other hand in order to obtain increased permeability the hollow fibre membrane has to be thinner. The thinner membrane, if there is no further mechanical strengthening, will be susceptible to damage much more easily, even in the event of a slight mechanical contact.

It is therefore the object of the invention to provide a semi-permeable multi-hollow fibre which is characterised by high permeability and improved mechanical strength and therefore allows easy handling.

It is a further object of the invention to provide an effective method for spinning a multi-hollow fibre with the aforementioned improved properties.

It is a further object of the invention to provide a spinning nozzle which is suitable for spinning such hollow fibres.

The multi-hollow fibre according to the invention has several separated hollow sections which extend along the entire axis of the fibre. Multi-hollow fibres of this kind can be manufactured by means of a method in which a solution of a polymer which is dissolved in a solvent, is extruded from several ring-shaped slits in a spinning nozzle which are arranged side by side wherein the extruded threads are gathered together in order to obtain one one-piece multi-hollow fibre. With the above method the second stage of gathering the extruded hollow fibres can be avoided if a spinning nozzle is used which has several independent openings for the injection of a first fluid (core fluid) and a corresponding number of ring slits surrounding independent openings wherein these ring slits are connected to one another to form one continuous slit for the extrusion of a second fluid (spinning fluid).

The invention thus provides a semi-permeable multi-hollow fibre of stable construction which can be spun in stable manner and can then be uniformly re-treated.

The invention further provides a semi-permeable multi-hollow fibre with excellent degree of efficiency with the selective separation of different molecular types and has a construction in which practically the entire external surface of the round wall of

each hollow fibre is brought actively into contact with a fluid flowing outside of the membrane.

The invention further provides a semi-permeable multi-hollow fibre which is characterised by excellent casting properties if namely the bundle of hollow fibres is cast with a casting material; to form a fluid-tight tubular base for fixing its two ends on a housing of the haemodialyser for the purpose of assembly, the casting material can easily penetrate between the fibres to form a leak-free tubular base and a tubular wall respectively.

The invention thus provides a semi-permeable hollow fibre having selective permeability which is provided with several separated hollow sections which extend in the longitudinal direction from one end to the other, wherein these thereby form one full-length through hole. A method for manufacturing semi-permeable multi-hollow fibres of this kind comprises extruding a spinning fluid or solution of a high polymer dissolved in a solvent through several ring slits which are arranged side by side and then gathering the separated hollow fibres which are extruded in this way in a condition capable of being connected or stuck.

A spinning nozzle for manufacturing this semi-permeable hollow fibre has several openings independent of one another for the injection of a first fluid (core fluid) and a corresponding number of ring slits which surround the individual openings wherein the ring slits are connected to one another to form one continuous slit for the extrusion of a secondl fluid (sleeve spinning fluid).

The invention will be explained in further detail with reference to the embodiments illustrated in the drawings. In the drawings:

Figure 1 shows in a cross-sectional and perspective view a multi-hollow fibre according to the invention;

Figure 2 shows in a cross-sectional and perspective view a different multi-hollow fibre according to the invention;

Figure 3 shows in a cross-sectional view a further multi-hollow fibre according to the invention;

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|---|---|
| Figure 4 | shows in a cross-sectional view a spinning nozzle for manufacturing the multi-hollow fibre according to Figure 1; |
| Figure 5 | shows in a cross-sectional view a spinning nozzle for manufacturing the multi-hollow fibre according to Figure 2; |
| Figure 6 | shows in a cross-sectional view a different spinning nozzle for manufacturing a multi-hollow fibre according to the invention which differs from that according to Figures 1, 2 and 3; |
| Figure 7 | shows in a cross-sectional view a further spinning nozzle for manufacturing a different multi-hollow fibre; |
| Figure 8 | shows in a cross-sectional view a different spinning nozzle for manufacturing a further multi-hollow fibre; |
| Figure 9 | shows in a cross-sectional view a multi-hollow fibre which is manufactured by means of the spinning nozzle according to Figure 7; |
| Figure 10 | shows in a cross-sectional view a further development of the spinning nozzle according to Figure 7; |
| Figure 11 | shows in a cross-sectional view a further development of the spinning nozzle according to Figure 8; |
| Figure 12 | shows in a longitudinal sectional view the spinning nozzle according to Figure 4 to illustrate the general construction thereof; |
| Figure 13 | shows in a longitudinal sectional view a different spinning nozzle to illustrate the general construction thereof; |
| Figure 14 | shows diagrammatically a method for spinning a multi-hollow fibre according to the invention; |
| Figure 15 | shows in a perspective view on an enlarged scale the duplication stage of the method according to Figure 14. |

The multi-hollow fibre according to the invention is provided in such a form wherein several separated hollow sections or spaces, preferably 2-4 hollow spaces, run from one end to the other wherein a full-length through hole is formed each time. With five and more hollow spaces the construction of the fibre becomes unstable and the spinning of such a multi-hollow fibre is not easy. Furthermore the after-treatments of the membrane in the processes which follow are difficult to carry out uniformly. Each hollow section in the multi-hollow fibre is preferably provided with a circular shape. Furthermore for a higher degree of efficiency in the case of selective separation the

hollow fibres are preferably gathered together in an arrangement where practically their entire exterior surface can be brought into active contact with a fluid flowing outside of the hollow fibre. Such a design can be achieved in that thickening of the membrane walls is avoided in the areas in which the hollow fibres are gathered together. Therefore the invention does indeed comprise a multi-hollow fibre 3 according to Figure 1 in which separated hollow sections 2 are provided inside the membrane walls 1 of a flattened fibre, but another hollow fibre 3, according to Figure 2 by way of example, is preferred in which the membrane walls 1 surround the individual separated hollow sections 2 and have a substantially uniform thickness wherein they are connected into one piece by way of a narrow joining area. The hollow fibre 3 according to Figure 2 has a shape in which one pair of conventional hollow fibres are gathered side by side in order to form one integral structural unit whereby they retain their original round surface area.

Another multi-hollow fibre according to the invention is obtained by gathering or sticking several hollow fibre units to one another in order to form one integral structural unit. Figure 3 shows one such multi-hollow fibre 3 which contains a pair of hollow fibre units. The above one-piece structural unit preferably has up to 10 hollow fibre units, preferably one pair of hollow fibre units. A multi-hollow fibre with 11 or more hollow fibre units is not particularly advantageous since during the assembly process of the dialyser the fluid-tight casting of the bundle of fibres with a housing is extremely difficult owing to the serious penetration of the casting material between the compressed fibres. This can be the cause of a blood leak. Furthermore for comfortable handling it is preferred if up to six hollow fibre units and preferably one pair of hollow fibre units are connected or stuck to one another in order to thus obtain a one-piece structural unit. A structural unit of this kind is preferably obtained if separated hollow fibres are stuck along their fibre axes, each having a precisely circular cross-section. The individual fibres which are stuck or connected to one another are therefore brought practically completely into contact with the external fluid. The combined fibres have a higher dialysis action than if they were separated and used independently of one another. The stuck or connected area 4 of the individual hollow fibres is preferably not extended too wide since such an area 4 reduces the effective surface area of these fibres in contact with the external fluid whereby a reduced dialysis action or performance would occur.

As explained above, with the multi-hollow fibre according to the invention individual hollow sections 2 are separated by a joining membrane wall which increases the mechanical strength. Therefore, even if the individual hollow fibres have thinner walls the multi-hollow fibre becomes more difficult to damage through external mechanical shocks whereby considerable bending forces can be withstood without breaking. The inventors have discovered that damage to the multi-hollow fibre as a result of external pressure or shock and the leaks arising from such damage are drastically reduced by using the multi-hollow fibre according to the invention. A multi-hollow fibre of this kind corresponds in its effect and performance to the corresponding number of hollow fibres of conventional construction wherein the former has a mechanical strength which amounts to two to four times that of the latter. As a result of the improved mechanical strength the multi-hollow fibre furthermore allows thinner membrane walls. According to the invention explained above it is possible to improve both the mechanical strength and also the dialysis performance and action of the hollow fibre.

A special feature of the invention is a unique spinning nozzle which differs from the conventional nozzles and which can be used for directly spinning a multi-hollow fibre of the aforementioned kind. This special spinning nozzle is characterised by a special construction in which several openings independent of one another are provided for injection of a first fluid (core fluid) and a corresponding number of ring-shaped slits are provided which surround the individual openings, with these ring slits communicating with one another to form one continuous slit for extrusion of a second fluid (sleeve spinning fluid).

A method for manufacturing a multi-hollow fibre according to the invention is explained below.

First special spinning nozzles according to the illustrations in Figures 4 and 5 respectively are used for manufacturing the multi-hollow fibre according to Figures 1 and 2 respectively. The standard method for manufacturing the conventional hollow fibre is to extrude a spinning fluid from a ring slit by using a spinning nozzle with a tube in an opening with simultaneous injection of a core fluid out from the inner tube.

In this case the ring slit and the inner tube are provided in a concentric arrangement. The spinning nozzles according to Figures 4 and 5 are provided with several separated round openings which are each formed by capillaries 6 for the injection of a core fluid wherein the capillaries 6 are surrounded by a ring chamber or slit 7 for the extrusion of a spinning fluid. The spinning nozzle which is used with the invention has the openings 5 used for injection of the core fluid arranged symmetrically or in a row. If by way of example three openings 5 are used then these can be arranged at the three corners of a regular or equilateral triangle, as shown in Figures 6, 8 and 11. In a similar way if four openings are provided then these can be arranged by way of example symmetrically at the four corners of a square.

The so-called dry-jet wet spinning is preferably used for spinning. This method is explained below with reference to the conventional spinning of hollow fibre from a cellulose-ester solution. In this case cellulose ester is dissolved in an organic solvent and is extruded as the sleeve solution from a ring slit of a dual-tube spinning nozzle (or a spinning nozzle with a tube in an opening), wherein a core fluid is simultaneously injected or ejected from an inner opening of the spinning nozzle. As an example of the core fluid it is possible to use a salt solution with a somewhat higher concentration, a solvent or an expanding agent for cellulose ester or a solution which contains the one, the other or both, or a liquid hydrocarbon with more than eight carbon molecules, such as a mono-cyclic terpene. In order to carry out the invention by using the aforesaid method a spinning fluid is extruded as mentioned from the ring spaces which surround several openings which are used for simultaneously injecting a core fluid, wherein the extrudates run in a vertical direction over a certain distance, preferably 50 to 1.000 mm, in an expansion space such as air, and then are introduced into a coagulating bath (by way of example into a water bath). The coagulated extrudates undergo in water a flushing process or step and are then wound onto a wind-up roller in the conventional manner. Obviously the invention is not restricted to the dry-jet wet spinning process but can also be used with so-called dry spinning, wet spinning and melt spinning. Furthermore the material for the multi-hollow fibre according to the invention is not restricted to cellulose acetate but can be selected from a large number of natural and synthetic polymer substances. For melt spinning it is namely possible to use not only the cellulose solution for the copper ammoniac method and the viscose solution, but also the solution of cellulose in

formaldehyde containing dimethyl sulphur oxide, solution of polymethylmethacrylate in acetone, aqueous polyvinyl alcohol solution, cellulose ester solution in dimethyl formamide, dimethylacetamide, dimethyl sulphur oxide, N-methyl-pyrrolidone and the like, molten polyamides and polyesters. Any high polymer composition or compound can be used for preparing the starting solution or the spinning fluid. By way of example it is possible to use polyacrylonitrile, acrylonitrile copolymers, polyvinylchloride, vinyl chloride copolymers including graft or block copolymers etc.

As explained above, in order to obtain an effective selective permeability it is necessary to form the multi-hollow fibre with such an arrangement that when used for separating substances in a fluid which flows through the hollow sections of the membrane it is in close proximity to the external fluid which flows in wide areas outside of the membrane. The spinning nozzles according to Figures 5 and 6 are therefore more advantageous than the spinning nozzle according to Figure 4 since the multi-hollow fibre thus formed has a larger more effective permeability area. With the conventional wet spinning method the design of the spinning nozzle directly determines the cross-sectional structure of the multi-hollow fibre spun therewith. As opposed to this with the dry jet wet spinning method in which the spinning fluid extruded by a spinning nozzle can run through a gas column before it is introduced into a coagulating bath the extruded spinning thread is easily changed in its form as a result of the action of its surface tension whereby the most stable arrangement is produced around a core fluid. The cross-sectional structure of the multi-hollow fibre therefore does not always correspond to the arrangement of the spinning nozzle used for spinning same. In order to achieve a better agreement between the two, new types of spinning nozzles are provided. The new types of spinning nozzles have several openings 5 for injecting a core fluid and a corresponding number of ring slits for extruding a spinning fluid. Each ring slit 7 surrounds one of these openings 5 wherein they are connected by means of one slit-like passage or by means of several such slit-like passages in symmetrical manner, as illustrated in Figures 7 to 11. The width of such slit-like passages 9 is preferably less than half and preferably less than a third of that of the ring-shaped slits 7. If the passages 9 are comparable with the width of the ring slits 7 then the multi-hollow fibre 3 being produced has a bone-shaped cross-section, as indicated by the dotted lines in Figure 9. The solid lines in Figure 9 show the cross-section of the hollow membrane or hollow fibre 3 which is manufactured by

using the spinning nozzle according to Figure 7 wherein two hollow fibres are connected to one another to form one piece by means of a connecting membrane 1a. It is evident that a significant correspondence exists between the cross-section of the fibre being produced and the design of the spinning nozzle being used since the slit-like passage 9 is narrow enough in this case. Furthermore the length 1 of the slit-like passage 9, as shown in Figure 7, is preferably less than half and more advantageously less than a third of the external diameter of the ring slits 7. If a longer slit-like passage 9 is used then the spinning fluid is extruded less uniformly around several hollow sections so that the multi-hollow fibre being produced is not uniform and no longer has a regular cross-section.

Furthermore with the spinning method which uses the above spinning nozzle with several openings for injecting a core fluid it was discovered that when a spinning nozzle is used in which the at least one slit-like passage 9 has an enlarged part in the centre layer 9a, as shown in Figures 10 and 11, the spinning fluid can be extruded very stably and uniformly around several hollow sections 7 whereby a multi-hollow fibre is produced with uniform concentric hollow fibre units which are gathered together. The enlarged part 9a of the slit-like passages 9 is preferably circular in cross-section, whereby the preferred diameter is equivalent to or less than the width of the ring slits for the extrusion of the spinning fluid. If such a spinning nozzle is used then the multi-hollow fibre is produced precisely matched with the construction of the spinning nozzle used.

As regards the spinning nozzles which are used by way of example for implementing the invention, the spinning nozzle 8 according to Figure 4 can in principle have the general construction according to Figure 12. A core fluid injection tube 6 ends in a pair of capillaries to form a pair of openings 5 for the injection of a core fluid, wherein these capillaries are surrounded by a narrow gap through walls of holes which are made in the base plate 10 in order to form ring slits 7 wherein the base plate is secured by means of a clamping ring 11. The core fluid injection tube 6 is thus arranged so that it passes centrally through a spinning fluid housing 12 whereby it is secured at the top to this housing 12 by means of a further clamping ring 13. The spinning fluid is fed through a pipe 14 into the housing 12 and then exits it through a filter 18 and is then extruded from the ring slits 7.

The invention also provides a novel method which can be used for the case where several hollow fibres are connected or stuck to one another to form one multi-hollow fibre, by way of example as illustrated in Figure 3. This method is unique in that a solution of cellulose ester in an organic solvent, as an example, is extruded from several independent ring slits wherein the extrudates are gathered in a connectable or stickable state in order to form one one-piece multi-hollow fibre.

This above method is explained in more detail below. To manufacture a specific multi-hollow fibre as illustrated in Figure 3 individual hollow fibre are spun and then gathered at the appropriate time in a stickable or connectable state. With the above example in which a cellulose ester solution is used for spinning, the “stickable state” is produced as follows.

For the case of a cellulose ester multi-hollow fibre the key factor of the “stickable state” lies in the immersion in a coagulating bath. During or immediately after the coagulation several hollow fibres are gathered in the coagulating bath wherein they then remain as a one-piece structural unit. They are then subjected to after treatments, such as rinsing and drying, and finally they are wound onto a wind-up roller. In this way a multi-hollow fibre is formed which has a predetermined number of cellulose ester hollow fibre units. In this case water alone or a mixture of water with a solvent or an expanding agent for cellulose ester can be used as the coagulating bath. In the case of a method which uses the solvent or the expanding agent in the bath the hollow fibres can be more effectively connected or stuck along the fibre axes. Furthermore the coagulating bath can be multi-phased. By way of example in a dual-phase coagulating bath hollow fibres can be gathered in the first phase of the bath which contains a comparatively large amount of solvent or expanding agent for a polymer used for the manufacture thereof, whereby then the gathered fibres move into the second phase of the bath which contains a lesser amount of such solvent or expanding agent.

The above method for gathering the hollow fibres in a coagulating bath is not restricted to cellulose ester fibres but can also be applied to other types of hollow fibres insofar as these are spun from a spinning solution or a spinning fluid.

Furthermore for hydrolysing the above cellulose ester hollow fibres for regenerating the cellulose hollow fibres a one-piece multi-cellulose ester hollow fibre can be hydrolyzed as it is. Furthermore in order to obtain regenerated cellulose multi-hollow fibres by means of hydrolysis, several cellulose ester hollow fibres can be hydrolyzed in the gathered state, or can be hydrolyzed individually wherein then the resulting hydrophilic fibres which are swollen with water are gathered together. Furthermore the invention can also be carried out by hydrolyzing the separated cellulose ester hollow fibres on at least their external surfaces whereby they are then introduced into a bath which contains a known cellulose plasticizer, such as glycerine, 1, 3-butandiole or propylene glycol in order to gather them together therein.

As explained previously above the multi-hollow fibre according to the invention which contains several hollow fibre units which are connected or stuck together in the longitudinal direction along the fibres, can be manufactured by spinning separated hollow fibres and gathering these together in a stickable state. As a result the individual hollow fibre components are originally independent of one another and are then stuck or connected next to one another in the longitudinal direction with a very ideal contact in which the connecting area or the sticking area is restricted in width and wherein the largest part of the fibre surface remains open. Furthermore with a different adhesion method according to the invention several hollow fibres which are spun separated from one another, are combined continuously with one another and treated in a bath which contains a solvent or an expanding agent for the polymer substance which is used for manufacturing such hollow fibres. By way of example in this case in which cellulose acetate is used as the polymer membrane material, several cellulose acetate hollow fibres can be combined continuously with one another and treated in a bath which contains acetone, α-pyrrolidone, formaldehyde, etc whereby they are gathered as explained previously. Or they can first be gathered together and then brought into contact with an aqueous solution which has a solvent or an expanding agent as explained above. In order to achieve such contact the hollow fibres can be treated in a bath or in another way, by way of example by means of a known method, in order to bring the hollow fibres into contact with a solution which is fairly widespread. By way of example a standard method for oiling the fibres can be used. Hollow fibres gathered together in this way are treated and then dried to obtain a multi-hollow fibre which has a predetermined number of hollow fibres which

are actively connected to one another or stuck to one another in the longitudinal direction.

The cross-section of the individual multi-hollow fibres of the type described above can be formed and modified in different ways, and the spinning nozzle used for the manufacture thereof can likewise be changed or redesigned. By way of example a modified spinning nozzle according to Figure 13 can be used for spinning a pair of separated hollow fibres which, as explained above, are then gathered together.

The invention is clearly apparent from the following specific examples and comparative examples.

Specific Example 1:

A spinning fluid with 26 parts cellulose acetate (type E-400-25 by Eastman Kodak), 44 parts acetone and 30 parts formamide was extruded from ring slits of a spinning nozzle with simultaneous injection of d-limonene as core fluid for spinning a multi-hollow fibre by means of the dry jet wet spinning method. The spinning nozzle used was of the structural type illustrated in Figure 7 with a pair of openings for injection of the core fluid. The capillary size of the core fluid injection openings 5 was 0.5 mm and the ring slits for the spinning fluid had an external diameter of 2.0 and an internal diameter of 1.5 mm, whereby the connecting slit 9 was 0.2 mm wide. The spinning fluid was extruded at a rate of flow of 11 ml/min, whilst the core fluid was injected at a rate of 13 ml/min. The thread extruded by the spinning nozzle ran 15 cm downwards into air before entering into a water bath in which it coagulated, was rinsed with water and then wound up onto a wind-up roller. The spinning speed was 100 m/min.

The cellulose acetate hollow fibre manufactured according to this example had a cross-section as illustrated in Figure 9 wherein a pair of hollow cores were provided which ran from end to end and formed the separated full-length through holes. It had a high mechanical strength with resistance to bending forces wherein a more comfortable handling could be predicted.

Specific example 2:

The same spinning fluid as in Example 1 was spun. The spinning nozzle had the same construction as in Figure 11. More particularly it had three openings 5 for injecting the core fluid wherein the slit-like passages 9 which joined the three ring slits for the spinning fluid had an enlarged part 9a with 0.4 mm diameter in the middle. The spinning fluid was extruded from the ring slits at a rate of 24 ml/min, whilst formamide was injected as core fluid at a rate of 30 ml/min. With this example a multi-hollow fibre was manufactured having three substantially concentric hollow fibres which are connected together.

Comparative example:

The same spinning fluid as in Example 1 was for spinning a hollow fibre extruded from a concentric dual-tube spinning nozzle of the conventional kind for the purpose of manufacturing a conventional hollow fibre. The spinning fluid was extruded at a rate of 5.5 ml/min and the core fluid was injected at a rate of 6.5 ml/min wherein the hollow fibre was wound onto a wind-up roller at a speed of 100 m/min. A hollow fibre with a circular cross-section was obtained in this way. The hollow fibre was compared with the multi-hollow fibre according to Examples 1 and 2 in terms of mechanical strength. The results were as follows:

| | Breaking strength (g/fibre) |
|---|---|
| Example 1 | 360 |
| Example 2 | 520 |
| Comparative example | 150 |

It was discovered that the multi-hollow fibre according to Examples 1 and 2 has a noticeable resistance to bending forces whilst the fibre of the comparative example has a much lower resistance in respect of these forces and can therefore be easily damaged .

Specific Example 3:

The same spinning method as in Example 1 was carried out for a solution of polymethyl methacrylate in acetone as the spinning fluid. A multi-hollow fibre with a pair of separated hollow sections was obtained in this way.

Specific Example 4:

The cellulose acetate multi-hollow fibres according to Examples 1 and 2 were immersed under tension in an aqueous solution with 20% $Na_2CO_3$ and 1% NaOH for hydrolysis for 45 minutes. The membranes were deacetylated in this way whereby two types of cellulose multi-hollow fibres were produced with two and three hollow sections respectively.

Specific Example 5:

The same spinning method as in Example 2 was applied using a solution of polyvinyl chloride in tetrahydrofurane as spinning fluid and dimethyl-sulphur oxide as core fluid. A multi-hollow fibre with three separated hollow sections was obtained in this way.

Specific Example 6:

A spinning fluid with 26 parts cellulose acetate (of type E-400-25 by Eastman Kodak), 44 parts acetone and 30 parts formamide was extruded from two independent ring slits of a spinning nozzle with one tube in an opening with simultaneous injection of d-limonene as core fluid for spinning a multi-hollow fibre by means of the dry-jet wet spinning method. A pair of hollow fibres which were extruded was passed down 15 cm in air for introduction into a coagulating water bath in which they were then gathered together, rinsed with water and then wound up onto a wind-up roller. Figure 14 shows the aforesaid spinning method illustrating the water bath for the coagulation. Figure 14 shows the core fluid tubes 20, spinning fluid tubes 21, dual-tube spinning nozzles 8 of a standard type, guide rods 22, a coagulating bath 23, a Y-shaped frame (creel) and a rinsing bath 25. Figure 15 shows on an enlarged scale the fibres when brought together. The cellulose acetate multi-hollow fibre manufactured with this embodiment was formed from a pair of hollow fibres stuck or connected actively to

one another so that it had a high mechanical strength and resistance to bending forces and was excellent to handle.

Specific Example 7:

A multi-hollow fibre was spun with the same spinning fluid and core fluid as in Example 6. The sole difference compared with Example 6 was that a mixture of water and acetone (75:25) was used as the coagulation bath and that three hollow fibres were brought together instead of two. With this example therefore a multi-hollow membrane was formed in which three hollow fibres were connected or stuck together actively side by side to form one one-piece structural unit.

Specific Example 8:

The multi-hollow fibre which had been manufactured according to Example 6 was used where a pair of cellulose acetate hollow fibres had been actively stuck to one another to form a one-piece structural unit. This was immersed whilst retaining fixed lengths in an aqueous solution of 10% $Na_2CO_3$ and 1% NaOH for 20 minutes at 30°C for the purpose of hydrolysis. The membrane was thereby substantially hydrolyzed for regeneration of the cellulose membrane. No change of shape was observed after hydrolysis, and a multi-hollow fibre was obtained in which a pair of cellulose hollow fibres are connected or stuck actively to one another.

Specific Example 9:

A spinning fluid with 28 parts cellulose acetate (of type E-400-25 by Eastman Kodak), 15 parts lactic acid, 15 parts α-pyrrolidone and 42 parts acetone was extruded with simultaneous injection of formamide as core fluid to spin a pair of cellulose acetate hollow fibres which were brought together by passing through a frame in a coagulation bath. The gathered hollow fibres were guided through a hydrolyzing bath with 10% $Na_2CO_3$ and 3% NaOH at 30°C where the fibres were stretched between a pair of rollers. In this way a regenerated cellulose multi-hollow

fibre was obtained which contained a pair of hollow fibre units which were stuck or connected actively to one another side by side to form a one-piece structural unit.

Specific Example 10:

A pair of cellulose acetate hollow fibres was manufactured by using spinning nozzles arranged side by side with one tube in an opening. The spun threads were introduced independently into the coagulating water bath without using the frame in order to form a pair of fibres which at this stage are not connected in one piece with one another. These fibres were introduced into a bath which was filled with an aqueous solution with 60% glycerine, where the fibres were guided through a frame, as in Example 9, in order to combine or connect them to one another with stretching. The combined hollow fibres were dried just as they were. In this way a multi-hollow fibre with a pair of hollow fibres which were stuck or connected actively to one another was obtained as a one-piece structural unit as in Example 9. Furthermore three cellulose acetate hollow fibres were brought together in a similar way in an aqueous glycerine bath whereby a multi-hollow fibre was produced which contained three hollow fibres which were effectively in one piece along the fibre axes.

Specific Example 11:

A pair of cellulose acetate hollow fibres was spun independently, as described in Example 10. After coagulation of the fibres they were brought together whereby the combined fibres were guided through an α-pyrrolidone/water bath (50:50) and then guided through a rinsing bath. The combined fibres were wound up on a wind-up roller as they were and then dried. The resulting multi-hollow fibre comprised a pair of hollow fibres stuck or connected to one another actively side by side. The fibres proved impossible to split, even under the action of considerable mechanical forces.

Specific Example 12:

Cellulose acetate hollow fibres were spun and gathered together, as in Example 11. They were then passed with slight pressure along the top side of a sponge roller which was driven slowly wherein its lower side was immersed into an acetone/water bath

(50:50) so that the rubber layer was fully soaked with aqueous acetone solution. After drying, the resulting multi-hollow fibre comprised a pair of hollow fibres which were stuck or connected actively to one another.

Specific Example 13:

A conventionally manufactured copper ammoniac spinning solution with a cellulose proportion 10.0 % by weight, ammonium proportion 7.0% by weight and copper proportion 3.6% by weight and a viscosity of 2.000 Poise (1 Poise $=10^{-1}$ $Ns/m^2$) was extruded through spinning nozzles with one tube in an opening (external diameter 5 mm) which were arranged next to one another, at a rate of 20 ml/min. At the same time tetrachloroethylene or d-limonene was extruded through a central core opening (1 mm diameter) at a rate of 5 ml/min. This sleeve/core compound fibre ran through an air column of 150 mm and was then introduced into a coagulation bath with an aqueous NaOH-solution with 11% by weight concentration at 250 ( accurately 25°C), where the incoming fibres were combined by means of a frame, as in the specific Example 6.

The delivery speed of the fibre through the coagulation bath was set at 100 m/min. The extent of normalization was about 30% (in the English text: normannrization).

The thus combined coagulated hollow fibre of threads was removed on a revolving or rotating string frame and held thereon for two hours. The string hung down from a rod and was rinsed sufficiently with fresh water by means of a spray shower. The string was then treated for regeneration in a diluted sulphuric acid bath with 3% by weight concentration and rinsed with fresh water. The thus treated string hung down from a moving frame and was moved through a tunnel drier for drying in a hot air atmosphere at 130°C. The string was finally and mechanically cut to the correct length for recovering the contained core fluid solvent and kept in a rest chamber at normal temperature for several hours.

The hollow fibres thus obtained had a combined form, there were namely two hollow fibres formed in one piece in the longitudinal direction, wherein each cross-section

along the axis of each of the hollow fibres was substantially constant, as shown in Figure 3

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Specific Example 14:

An acrylonitrile copolymer with 94% acrylonitrile and 6% methylacrylate (inherent viscosity in dimethyl formamide: 1.6) was dissolved in a 70% nitric acid at -5°C. The solution was spun by using spinning nozzles with one tube in an opening which were arranged very close to one another. A 35% nitric acid solution was used as the core fluid. The two spun compound threads were introduced over an air gap of 180 mm into a 35% nitric acid bath in which the two threads were combined by means of a frame. The combined threads were then introduced into the next bath which contained 20% nitric acid. The threads were then passed through the water bath for the purpose of washing and then wound-up onto a roller. The wound-up fibre on the roller was then disposed in the water bath for the purpose of fundamental cleaning. After drying, the fibres were cut to predetermined lengths. The hollow fibre obtained was precisely the same as shown in Figure 3.

Obviously numerous other embodiments are possible.